Modeling Interface Diffusion as a Mechanism for Threshold Voltage Drift in pH Sensors

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Abstract—**In this work, we highlight the importance of interface diffusion in determining the performance of a class of biosensors. Diffusion along interfaces is proposed as a mechanism for charge transport and drift in the threshold voltage of Ion Sensitive Field Effect Transistors (ISFETs). A general model is developed for the case of an ISFET with a single insulating material. We study the effect of interface diffusion and its impact on the overall response of these sensors. The interface charge build up is obtained using the developed model and the drift in the threshold voltage with time is calculated. The developed model is simulated using finite difference method. The reduction in time for charge build up at the insulator-semiconductor interface is highlighted using the proposed mechanism and compared with the results of existing mechanisms. The results obtained are similar to experimental data available in literature, and show that the presence of the proposed method of charge transport will play a crucial role in deciding the transient response and long term drift in ISFET performance.**

I. INTRODUCTION

Over the last few years, research on the development and modeling of solid state sensors for biological applications has progressed rapidly. It has been mainly driven by the large number of potential applications for these devices. With the advances in fabrication technology, it has been possible to miniaturize most semiconductor devices including sensors. Different types of biosensors, based on various sensing mechanisms, have been studied over the years [1] – [5]. Ironically, this enormous research output has not been leveraged for commercial production due to various factors. One important factor has been the drift in performance with time. In this work, we model a mechanism, which has so far been ignored, for drift in the threshold voltage.

pH sensors are an important class of biosensors as they form the building blocks of promising applications like Lab-on-chip systems, and a complete understanding of all relevant phenomena associated with pH sensors is essential. Ion Sensitive Field Effect Transistor (ISFET) is a kind of pH sensor that has been studied and modeled by many researchers [1] – [3]. Moreover, it is representative of most solid-state chemical sensors and hence, it will be used for discussion here. For pH sensing, the integration of a Reference Field Effect Transistor (REFET) along with the ISFET has been an essential development that has enabled miniaturization of the pH sensor by overcoming the need for a conventional reference electrode [2], [3]. An important thrust for improvement in the development and understanding of ISFET theory has been its similarity to the MOSFET. Hence all electrical phenomena associated with MOSFETs, are directly used for understanding the processes at the Insulator–Semiconductor interface and the channel between the source and drain of the ISFET. In order to understand the instantaneous response mechanism of the ISFET, several researchers have studied the mechanisms at the Electrolyte–Insulator–Semiconductor (EIS) interface [6]–[10].

In [11],[12], attempts to model drift have been made qualitatively, considering the variation in the capacitance of the insulator material due to chemical modifications in the surface layer facilitated by dispersive transport mechanisms like hydration. The model developed is specific to the insulator material. The main source of disparity in this theory is as follows. Based on experimental measurements made in [12], it is clear that drift is not affected by the presence or absence of the electric field between the gate (reference) electrode and the semiconductor bulk. This gives an impression that the diffusing species is effectively neutral. It is also clearly established in [11] and [12] that the maximum threshold voltage drift increases with pH for n-channel ISFETs. Hence, it was concluded that the diffusing species was probably linked to the hydroxyl ion. This leads to a conflict on the nature of the diffusing species inferred from two different experimental results using the same device. Moreover, the exact diffusing species is not yet clear. Therefore, additional charge transport mechanisms are needed to completely account for drift in the threshold voltage.

We propose that there is an inherent additional charge transport mechanism that accounts for drift and presents an improvement over the current understanding of threshold voltage variations in an ISFET. All existing models for drift have not considered the mechanism of interface diffusion. In this work, a model is developed for calculating the nature of pH response arising from interface diffusion and is examined with the contribution due to bulk diffusion. The magnitude of

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charge build up at the insulator–semiconductor interface resulting from the proposed model is compared with that of the existing model for drift. We describe in detail, the salient points of the finite difference method used in simulation and analyze how the proposed mechanism clearly describes the process of long term drift and its importance with respect to the use of a REFET. Areas of application of the proposed mechanism and implications have been outlined in the concluding sections of this work. The possible remedies for restricting long term drift are also discussed in the last section.

II. MODELING

A. *Interface diffusion*

The discontinuities in the lattice structure at all interfaces allow enhanced diffusion rates enabled by a large number of imperfections [13]. An analytical model for the process of interface diffusion has been developed by Fisher and in this model, the interface between two lattices is called the boundary region and is assumed to be of uniform thickness [13]. There are three separate regions of interest: the bulk of material 1 with concentration c_1 and diffusion constant D_1, the boundary with concentration c' and diffusion constant D' and the material 2 with concentration c_2 and diffusion constant D_2. The process of diffusion in 3D is described by Fick's second law which is given as [13],

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{1}$$

where c is the concentration of the diffusing species and D is the diffusion constant. The diffusion constant at the boundaries has a much greater value compared to the bulk diffusion constant ($D' >> D$) [13]. The boundary conditions at the interface of the boundary region and the bulk material are given by,

$$c' = c \tag{2}$$

$$D'\frac{\partial c'}{\partial n} = D\frac{\partial c}{\partial n} \tag{3}$$

where n is the direction normal to the interface plane. In general, the diffusing species can be broadly classified into three different types: positive ions, negative ions and neutral molecules. The exact concentration of different ions and molecules near the electrolyte–insulator interface is largely different from their bulk concentrations. Even with the aid of experimental measurement and results, the exact diffusing species has not been clearly established. Hence, in this work, a generic model is developed without restricting the exact diffusing species.

In the working conditions of ISFETs, the top surface of the insulator is exposed to the electrolyte and the surface concentration of various ions, as mentioned earlier, is decided by the nature of charge distribution resulting from the formation of an electrical double layer. The surface concentration of H^+ ions is obtained from the pH value as,

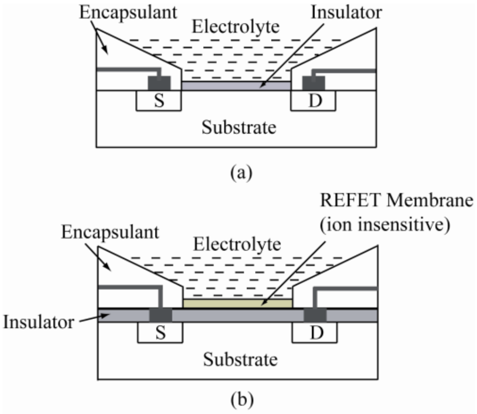

Fig. 1. The generalized cross section of (a) ISFET (b) REFET.

$$c_s = \frac{10^{-pH} N_a}{1000} \tag{4}$$

where N_a is the Avogadro Number. The factor of 1000 is used to obtain the value of c_s in units of cm^{-3}. Similarly, the surface concentration of OH^- ions can be written as,

$$c_s = \frac{10^{pH-14} N_a}{1000} \tag{5}$$

While the exact diffusing species may be different from either the hydrogen ion or the hydroxyl ion, (4) and (5) will be used as a guideline for estimating the rough order of concentration of the diffusing species in the electrolyte. The surface concentration, c_s, is assumed to be always a constant. Along all the sides of the insulator there are interface boundaries for charge transport from the electrolyte to the insulator–semiconductor interface and (1) through (3) are valid at all interface boundaries. Fig. 1(a) shows a representative configuration of the general ISFET structure. Fig. 1(b) is a schematic of a commonly used REFET structure. Even an ideal REFET membrane, that is totally insensitive to ions, will enable interface boundary diffusion along its interface with the encapsulation material and hence, the threshold voltage drift due to interface diffusion cannot be checked by replacing the ion insensitive coating. The mechanism of interface diffusion becomes more prominent with the presence of more number of interfaces for diffusion. We focus our attention to interfaces where charge accumulation alters the threshold voltage and leads to drift. Fig. 2 shows the structure of the proposed model with the interface boundaries for the schematic shown in fig. 1(a). The interface boundary is assumed to be of thickness δ along all interfaces and the length L and width W of the insulator are assumed to be same as dimensions of the channel for the sake of simplicity. t_{ox} is the thickness of the insulator material.

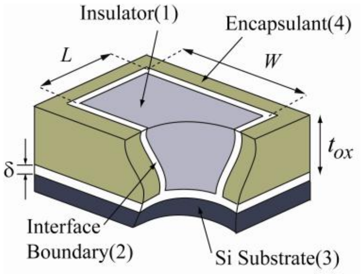

Fig. 2. The structure of the ISFET with the interface regions.

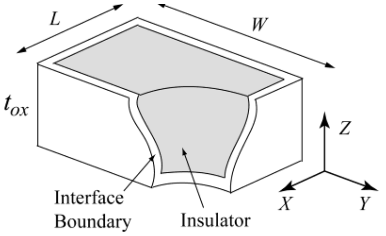

Fig. 3. Simplified interface structure used in simulations.

B. *Threshold Voltage*

The ions present in the electrolyte, diffuse into the insulator material through the bulk and through the interface boundary. The process continues till there is no concentration gradient at any point in the system. The accumulation of charge at the interface between regions 1–3, called the interface charge, leads to a variation in threshold voltage which is given by,

$$|\Delta V_t| = \frac{Q^I}{C^I} \tag{6}$$

where Q^I is the total interface charge per unit area and C^I is the insulator capacitance per unit area. The expression for threshold voltage variation given by (6) is also used in the case of REFET where Q^I will be the interface charge between the ion insensitive membrane and the insulator. In the presence of multiple interfaces, between the electrolyte and the channel, (6) has to be modified as

$$|\Delta V_t| = \frac{\sum_{i=1}^{m} Q_i^I}{C_{eq}} \tag{7}$$

where m is the number of interfaces and C_{eq} is the equivalent capacitances of all layers. In (6) and (7), the contribution of charges in the bulk of the insulator material is assumed to be negligible because the process of bulk diffusion proceeds at a much smaller rate compared to boundary diffusion. The exact contribution of charges along the interfaces between regions 1–4, shown in fig. 2, is not considered in the present model. The simulation of the developed model is carried out and results are presented in the following section.

III. SIMULATION

The model is simulated using C and is formulated using the simple explicit method of finite difference approximations to derive numerical solutions of the 3D diffusion equation described in (1). The model in fig. 2 was simplified by assuming that the there is no bulk diffusion in the encapsulation material as its primary function is to prohibit the occurrence of such processes. In order to reduce the complexity, the interface boundary between the encapsulation material and the substrate (between 4 and 3) is considered to be absent. These simplifications lead to the modified structure shown in fig. 3. The whole structure is made discrete by considering it to be made of a number of nodes in all three dimensions. All points in the bulk and the interface boundary are assumed to have no initial concentration of charges and the surface concentration has been assumed to remain uniform throughout and time invariant for a given pH. The gap between adjacent nodes in the x, y, z directions are Δx, Δy, Δz and for the stability and convergence of the used method, the size of the time steps, Δt, has to satisfy the stability criterion which is given by[14],

$$D\Delta t\left(\frac{1}{\Delta x^2}+\frac{1}{\Delta y^2}+\frac{1}{\Delta z^2}\right) \le \frac{1}{2} \tag{8}$$

For simulations, the value of Length, L is taken as 1μm and the width, W, is taken to be 1μm. The insulator material is assumed to be SiO_2 and is 100 nm thick. We assume the bulk diffusion coefficient value for H^+ ions along SiO_2 interface boundary is $\sim 10^{-15} cm^2/s$ [15] and the interface boundary diffusion coefficient to be two orders higher in magnitude [16]. For the sake of numerical calculations, we will assume that this diffusion constant is representative of the diffusing species, though the actual value depends on the exact diffusing ion. In calculations, δ is assumed to be 0.5 nm [16]. The structure is considered to be made up of 20 nodes along the depth of the insulator, 50 nodes along the length and 50 nodes along the width to facilitate reduction in simulation time and satisfy (8). The concentration of the diffusing species along the depth of the interface boundary is simulated and shown in

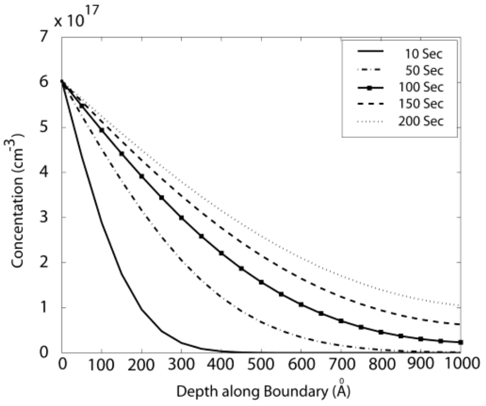

Fig. 4. Concentration profiles along the depth of the interface boundary, from the surface to the insulator-semiconductor interface, at various instants of time.

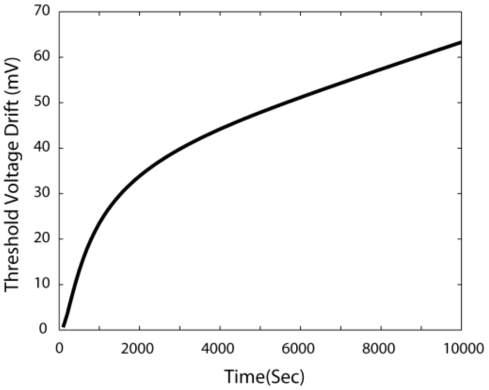

Fig. 5. Simulated drift in the threshold voltage considering both interface and bulk diffusion.

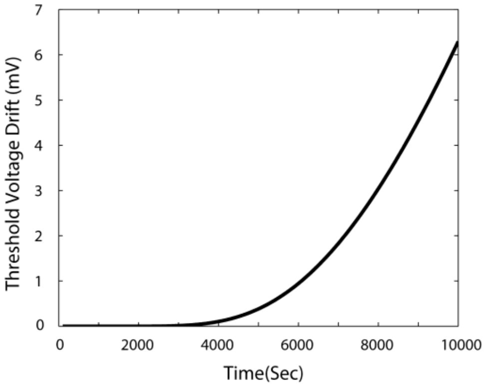

Fig. 6. Simulated drift in the threshold voltage considering only bulk diffusion.

fig. 4 for a surface concentration of $6{\times}10^{17}\text{cm}^{-3}$, which represents the general order of the surface concentration of ionic species (this value corresponds to the [OH^-] for pH = 11 using (5)). It can be seen from fig. 4 that a significant concentration has developed at the depth of 100nm after the completion of 100 seconds. The drift in threshold voltage due to the accrual of interface charge is calculated using (7) and is shown in fig. 5. The calculated steady state value of drift from (5) and (7) is 140.5 mV. The nature of drift shows good correlation with experimentally observed transient drift reported in [2]. The values of threshold voltage drift due to interface charge considering only bulk diffusion as proposed in earlier literature, is plotted for the same surface concentration in fig. 6. Comparing plots from fig. 5 and fig. 6, it is clearly seen that the process of interface diffusion is the greater contributor to drift compared to bulk diffusion.

IV. CONCLUSION

An analytical model for drift has been developed considering the process of interface boundary diffusion. It has also been shown using simulations that the proposed refinement of the existing drift model is essential. The process of interface boundary diffusion severely limits the use of the ISFET in conditions with high surface concentration of the diffusing species (for eg., pH>11 when OH^- is the diffusing ion and pH<3 with H^+ as the diffusing ion) and also plays a pivotal role in the response of REFET. The response time also affects the transient performance of the device if the interface charging-discharging cycle is also a slow process. To counter drift, the proposed model suggests a restriction on the use of multiple layers in the insulator material when there is a direct interface diffusion path to each of the interfaces from the electrolyte. Dispersive transport models with hopping mechanisms and limited interface-site vacancies can be used to improve the current model.

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